

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		51009/0114 U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5) <b>09/214840</b>
INTERNATIONAL APPLICATION NO. PCT/EP97/03530	INTERNATIONAL FILING DATE July 4, 1997	PRIORITY DATE CLAIMED July 15, 1996
TITLE OF INVENTION MOULDED ARTICLES OF CELLULOSE HYDRATE WITH ENZYMATIALLY MODIFIED SURFACE		
APPLICANT(S) FOR DO/EO/US Klaus-Dieter HAMMER, Martina KOENIG, and Theo KRAMS		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US)</p> <p>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371 (c)(2)).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11. to 16. below concern other document(s) or information included:</p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input type="checkbox"/> Other items or information:</p>		

17.  The following fees are submitted:**Basic National Fee (37 CFR 1.492(a)(1)-(5):**

Search Report has been prepared by the EPO or IPO .....	\$840.00
International preliminary examination fee paid to USPTO (37 CFR 1.482) .....	\$670.00
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) .....	\$760.00

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....	\$970.00
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International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) .....	\$96.00
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<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>	\$ 840.00
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Surcharge of \$130.00 for furnishing the oath or declaration later than	<input type="checkbox"/> 20	<input type="checkbox"/> 30	\$ 0.00
months from the earliest claimed priority date (37 CFR 1.492(e))			

Claims	Number Filed	Number Extra	Rate
Total Claims	12	-20 =	\$ 0 X \$18.00 \$ 0.00
Independent Claims	2	-3 =	\$ 0 X \$78.00 \$ 0.00
Multiple dependent claim(s) (if applicable)			+ \$260.00 \$ 0.00

<b>TOTAL OF ABOVE CALCULATIONS =</b>	\$ 0.00
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Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).	\$ 0.00
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<b>SUBTOTAL =</b>	\$ 840.00
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Processing fee of \$130.00 for furnishing English translation later than	<input type="checkbox"/> 20	<input type="checkbox"/> 30	\$ 0.00
months from the earliest claimed priority date (37 CFR 1.492(f)).			+ \$ 0.00

<b>TOTAL NATIONAL FEE =</b>	\$ 840.00
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +	\$ 40.00
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<b>TOTAL FEES ENCLOSED =</b>	\$ 880.00
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Amount to be: refunded \$ charged \$
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- a.  A check in the amount of \$880.00 to cover the above fees is enclosed.
- b.  Please charge my Deposit Account No. 19-0741 in the amount of \$ to the above fees. A duplicate copy of this sheet is enclosed.
- c.  The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 19-0741. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

SIGNATURE

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REGISTRATION NUMBER

09/214840

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No. 051009/0114

In re patent application of

Klaus Dieter HAMMER et al.

Serial No. Unassigned

Filed: January 13, 1999

For: MOULDED ARTICLES OF CELLULOSE HYDRATE WITH  
ENZYMATICALLY MODIFIED SURFACE

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application, Applicants respectfully request that the following amendments be entered into the application:

IN THE CLAIMS:

Claim 11, lines 1 and 2, delete "or 10".

Claim 12, line 2, delete "one or more of claims 9 to 11", and insert --claim 9--.

REMARKS

Applicants respectfully request that the foregoing amendments to Claims 11 and 12 be entered in order to avoid this application incurring a surcharge for the presence of one or more multiple dependent claims.

Respectfully submitted,

January 13, 1999

  
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Moulded articles of cellulose hydrate with enzymatically modified surface

The invention relates to shaped articles based on  
5 hydrated cellulose and to a process for the treatment of  
the surface of such shaped articles. The tubular shaped  
articles are particularly suitable as foodstuff casings,  
specifically as sausage skins.

10 The production of hydrated cellulose shaped articles by  
the viscose process has been known for a long time. In  
this process, an aqueous solution of cellulose xantho-  
genate is extruded into an acid precipitating bath. It is  
regenerated there to hydrated cellulose. The hydrated  
15 cellulose is initially present here in the gel state. A  
seamless, tubular shaped article is obtained if the  
viscose solution is extruded through an annular die.  
Hydrated cellulose shaped articles can also be produced  
by other processes, for example by the copper  
20 oxide/ammonia process (superseeded industrially) or the  
amine oxide process using N-methylmorpholine N-oxide (DE-  
A 196 07 953).

The tubular sausage casings based on hydrated cellulose  
25 which are produced in this way are often treated with  
various preparations on the inside and/or outside,  
according to the envisaged end use. For example, blood  
sausage adheres very firmly to the hydrated cellulose  
casing. So that the casing can nevertheless be peeled off  
30 easily, without thereby tearing open the frying surface,  
it is provided with a release preparation on the inside.  
A suitable release preparation comprises, for example, a  
chromium-fatty acid complex compound and a dialkyl-  
polysiloxane. Long-life frying sausage, on the other  
35 hand, has the tendency to become detached from the cellu-  
lose casing in the course of time. The adherence between

the frying sausage and casing is therefore increased with an appropriate internal preparation. The adherence preparation also comprises a water-insoluble cured cationic resin and an oil. The oil here may be a vegetable oil, a  
5 triglyceride mixture of plant fatty acids, a paraffin oil or a silicone oil. Other preparations serve to make the cellulose casing resistant to attack by mold. Di-n-decyl-dimethyl-ammonium salts, for example, are employed as fungicidal agents. Other preparations comprise a resin  
10 and particles or fibers of plastic or cellulose. They provide a rough surface.

Internal and external preparations are generally applied to the cellulose gel tube. However, the application here

15 is not always uniform. It depends on the degree of swelling and on the water content of the hydrated cellulose gel tube, and also on the nature of the device employed for the application. The squeeze rolls arranged before the dryer can furthermore cause folds. In general,  
20 the application becomes less uniform the smoother the surface. In the case of the fiber-reinforced casings, the surface becomes smoother if more viscose solution has been applied. The surface of such smooth sausage casings must be roughened with an appropriate external preparation  
25 so that, after watering, this casing can be pushed onto the filling pipe even with greasy hands. A non-uniform, streaky application of the external preparation would make handling more difficult.

30 The object was therefore to provide a process with which the surface of hydrated cellulose shaped articles can be roughened to a more or less pronounced extent as desired, so that an external preparation to increase the roughness is no longer necessary. Furthermore, the customary  
35 internal and external preparations should be distributed more uniformly over the surface and adhere better.

The object is achieved by treating the flat or tubular hydrated cellulose shaped article, preferably in the gel state, with a cellulase over a defined period of time. "Flat shaped article" is to be understood in general  
5 terms as meaning a flat film.

The present invention thus relates to a process for the treatment of flat or tubular hydrated cellulose shaped articles, in particular foodstuff casings, which comprises allowing at least one cellulase to act on the surface and then inactivating this cellulase permanently.  
10

The present invention also relates to flat or tubular shaped articles, in particular foodstuff casings, based on hydrated cellulose, the surface of which is modified by the time-limited action of at least one cellulase. They can be produced by any desired process, but preferably by the viscose or amine oxide process.  
15

There are cellulases which exhibit their highest activity in a slightly acid environment (pH 4.5 to 5.5) and those which are particularly active in a virtually neutral environment (pH 6 to 7). Both types of cellulases can be used in the present process. They are usually prepared  
20 from *Aspergillus* or *Trichoderma* species. The cellulase should accordingly act on the shaped article at a pH in the range from 4.0 to 7.5, preferably from 4.5 to 7.0. The cellulases are inactivated permanently by increasing the pH to more than 8. The same effect is achieved if the  
25 temperature rises to more than 70°C. A temperature of more than 70°C is usually reached during the drying step customary in the viscose or amine oxide process. Additional heating of the cellulose shaped article is therefore not necessary as a rule.  
30

In general, the cellulase is allowed to act on the hydrated cellulose shaped articles for 20 seconds to 40 minutes, preferably 2 minutes to 20 minutes. The surface roughness increases with the duration of the

- 5 action. The temperature here is 50 to 68°C, preferably up to 60°C. The enzyme develops its highest activity at this temperature. Below 50°C, the degradation process effected by the cellulase is slowed down and the action time must then be correspondingly longer. It has proved favorable  
10 to employ aqueous solutions with a content of 0.2 to 20% by weight, preferably 0.5 to 5% by weight, of cellulase, based on the total weight of the solution.

Tubular hydrated cellulose shaped articles can be treated

- 15 with the enzyme solution on the inside and/or outside. By appropriate adjustment of the cellulase concentration in the internal and external bath, it is also possible to achieve a roughness on the inside which differs from that on the outside. The shaped articles treated with enzyme  
20 are recognizable by a more or less smooth surface. The process according to the invention can be used for pure, that is to say not fiber-reinforced, hydrated cellulose casings, but also equally well for fiber-reinforced hydrated cellulose casings. The fiber-reinforced casings  
25 are produced by applying the viscose solution to the fiber reinforcement from the outside, from the inside or from both sides. The casings produced in this way are accordingly called externally viscosed, internally viscosed or double-viscosed casings. The fiber reinforcement  
30 usually comprises a hemp fiber nonwoven. The cellulase-treated casings which are not fiber-reinforced usually have an opaque appearance.

The viscose solution may also comprise various additives,

- 35 such as alginate. The content of these additives may be up to 30% by weight, based on the total weight of the

viscose solution. The properties of the shaped articles, in particular the mechanical properties, can therefore be modified further.

- 5 Enzymes having a cellulolytic action are generally feared in the meat products sector and everything has been done to avoid their occurrence. In the maturation of long-life sausages, they can be formed by certain molds and yeasts under adverse climatic conditions and can cause hydrated  
10 cellulose casings to be severely damaged or even destroyed. This applies even to fiber-reinforced casings. Damaged casings can be removed from the frying sausage only with great difficulty and also only in shreds.
- 15 On the basis of the abovementioned action, such enzymes were excluded from the production of foodstuff casings, in particular sausage casings. In the search for alternatives for rough surface preparation of fiber casings and matting of pure hydrated cellulose casings,  
20 the decision to employ the destructive properties of enzymes in a targeted and controlled manner to achieve specific surface effects took shape.

- The enzyme treatment can be integrated into various  
25 phases of the viscose or amine oxide process. They can act on the cellulose shaped articles while these are still in the gel state. The casings produced by the viscose process have a swelling value of about 200 to 220%, while those produced by the amine oxide process  
30 have a swelling value of up to 320%. The enzymes can then also reach deeper zones. Within a shorter period of time and/or at a lower enzyme concentration (up to 3% by weight of cellulase, based on the total weight of the enzyme-containing solution), significant roughening  
35 effects can already be achieved. The cellulase treatment can be integrated best, and above all without high

industrial outlay, in this phase. The enzyme treatment can also be combined with a secondary plasticizing. The secondary plasticizer is primarily glycerol.

- 5 However, it is also possible to pass the already dried hydrated cellulose shaped articles through the enzyme bath or to spray them with the enzyme solution. After the drying, the swelling value has fallen to about 130 to 140% in the case of the casings produced by the viscose process, and to about 180% in the case of those produced by the amine oxide process. The hydrated cellulose has assumed a denser structure. Subsequent cellulolytic degradation therefore takes place predominantly on the surface, and to a lesser extent depthwise.
- 10
- 15 The enzyme which has been inactivated by heat and/or alkali can be used at the same time as an adhesive impregnation. Like other proteins, it can be bonded to the cellulose by customary curing or crosslinking agents.
- 20
- 25 The tubular foodstuff casings produced by the process according to the invention exhibit the further advantage that the internal or external preparations described above can be applied considerably better and more uniformly. More of these adhere, so that significantly better effects can be achieved with smaller application amounts. Because of the roughened surface structure, the casings are easier to print on. This is particularly important for sausage casings which are printed by the
- 30 flexographic printing process. Long sections of the casings according to the invention can also easily be pushed onto the filling pipe in the watered state without an additional coating being necessary to increase the roughness. Finally, gathering (= accumulation) of the
- 35 tubular casing in sections is also facilitated.

The following examples are intended to illustrate the invention without limiting it in any way.

Example 1:

- 5 An externally viscosed hydrated cellulose tube of caliber 48 (= 48 mm diameter) was passed in the gel state through a plasticizer vat which contained, per liter, 100 g of glycerol, 25 g of cellulase (\*Cellusoft L from Novo Nordisk A/S, Bagsvaerd, Denmark) and water as the remainder and had a pH of 6 to 7 and a temperature of 50 to  
10 60°C. The residence time in this vat was 10 min. Thereafter, the water adhering to the surface was stripped off. The tubular casing was then provided with a customary adhesive impregnation on the inside. The tube  
15 was then inflated to the caliber with air ("supporting air") and dried with hot air down to a residual moisture content of 8 to 10% by weight, based on the total weight. The outer surface was rough and matt. No difference from the casings which had not been treated with enzyme was  
20 found in the mechanical properties, in particular the strength. Because of the rough surface, the watered casing sections could be separated from one another easily and pulled up onto the filling pipe. The filling operation itself, the maturing process and the ease of  
25 peeling corresponded to a casing which had not been treated with enzyme.

Example 2:

- 30 A double-viscosed, fiber-reinforced hydrated cellulose gel tube of caliber 60, in which 40% of the viscose solution was applied to the fiber nonwoven from the outside and 60% of the viscose solution was applied from the inside, was treated on the inside and outside with a solution which contained, per liter, 100 g of glycerol,  
35 30 g of \*Cellusoft L and water as the remainder. The pH of the solution was 6 to 7 and its temperature was 50 to

60°C. The duration of treatment was 20 minutes. The tube was freed from the adhering residues of solution by squeezing off with the aid of a pair of rolls and was then deposited in a container. Before intake into the  
5 dryer, the tube was finally also impregnated with a 2% strength by weight aqueous glyoxal solution. The enzyme-protein was firmly bonded to the cellulose surface in this manner and thus resulted in an adhesive impregnation. The tube was then dried in the inflated state at  
10 above 70°C until the residual moisture content was 8 to 10% by weight. It was rough and opaque.

Long watered sections could be pushed effortlessly onto the filling pipe. The casing was then filled with long-life frying sausage. Even after a long period of maturation,  
15 the casing still adhered adequately and uniformly to the frying sausage. At the end of the maturation process, the casings could be peeled off without any difficulty. The ease of peeling was evaluated as "2.5"  
20 (subjective scale from 1 to 6; 1 = can be peeled off very easily, 6 = can be peeled off only by destroying the casing or tearing open the frying surface).

Example 3:

25 A hydrated cellulose gel tube of caliber 40 was passed through a plasticizer vat which contained, per liter, 100 g of glycerol, 15 g of <sup>®</sup>Cellusoft L and water as the remainder. The pH was again 6 to 7, but the temperature was 60 to 65°C. The duration of action was shortened to  
30 5 minutes. Excess treatment solution was squeezed off as described. The casing was then inflated to the caliber with air and dried with hot air to a residual moisture content of 8 to 10% by weight. The casing was then gathered into worms in sections, the moisture content being increased to 14 to 16% by weight. The outer surface  
35 was rough and matt. Owing to the enzyme treatment, the

behavior of the casing during filling had improved significantly. The filling caliber varies to a lesser degree than in casings which had not been treated with enzyme. The other mechanical properties were in the usual range.

Example 4:

A hydrated cellulose gel tube of caliber 38 which had been colored brown was passed through a plasticizer vat  
which contained, per liter, 100 g of glycerol, 20 g of  
\*Cellusoft L and water as the remainder. The pH and  
temperature of the treatment solution were as stated in  
Example 3. The residence time of the tube in the vat was  
2 minutes. Excess solution was squeezed off again. During  
subsequent drying with hot air, the tube was passed  
helically over a roll and in this way converted into a  
wreath shape. The surface of the finished casing was  
rough and matt. The mechanical properties of the tube  
were not impaired.

20

Patent Claims

1. A process for the treatment of flat or tubular hydrated cellulose shaped articles, which comprises  
5 allowing at least one cellulase to act on the surface and then inactivating this cellulase permanently.
2. The process as claimed in claim 1, wherein the cellulase is allowed to act at a pH in the range  
10 from 4.0 to 7.5, preferably 4.5 to 7.0.
3. The process as claimed in claim 1, wherein the cellulase is inactivated by increasing the pH to  
15 more than 8 and/or increasing the temperature to more than 70°C.
4. The process as claimed in claim 1, wherein the cellulase is allowed to act at a temperature of 50 to  
20 68°C, preferably up to 60°C, for 20 seconds to 40 minutes, preferably 2 minutes to 20 minutes.
5. The process as claimed in claim 1, wherein the cellulase is employed in the form of an aqueous solution with a content of 0.2 to 20% by weight, preferably 0.5 to 5% by weight, of cellulase, based  
25 on the total weight of the solution.
6. A flat or tubular shaped article based on hydrated cellulose, the surface of which is modified by the time-limited action of at least one cellulase.  
30
7. The shaped article as claimed in claim 6, which is produced by the viscose or amine oxide process and on which the cellulase has acted while the cellulose was still in the gel state.  
35

8. The shaped article as claimed in claim 6, which is produced by the viscose or amine oxide process and on which the cellulase has acted after the cellulose has been regenerated and dried.

5

9. The tubular shaped article as claimed in claim 6, which is modified by the action of the cellulase on the inside and/or outside.

10 10. The tubular shaped article as claimed in claim 9, which has subsequently been subjected to the action of a fungicidal solution and/or a release or adhesive preparation.

15 11. The tubular shaped article as claimed in claim 9 or 10, which is reinforced with a fiber nonwoven, preferably of hemp fibers.

20 12. The use of a tubular shaped article as claimed in one or more of claims 9 to 11 as a foodstuff casing, preferably as a sausage skin.

Abstract:

Moulded articles of cellulose hydrate with enzymatically modified surface

The invention relates to a process for the treatment, in particular for the roughening, of the surface of hydrated cellulose shaped articles, in which at least one cellulase is allowed to act on the surface and is then inactivated permanently. The tubular films modified in this way are particularly suitable as foodstuff casings, specifically as sausage casings.

Cellulose-based food casings produced by the amine oxide process

The invention relates to flat or tubular cellulose-based  
5 food casings which are produced by extruding ("spinning")  
cellulose dissolved in N-methylmorpholine N-oxide. The  
casings are particularly suitable as sausage casings.

Cellulose is insoluble in the usual solvents. It does not  
10 have a melting point or melting range and cannot  
therefore be melt-processed either. Therefore, it is  
usually chemically modified for producing food casings.  
However, these processes are associated with a breakdown  
15 of the cellulose, i.e. the mean degree of polymerization  
of the cellulose becomes lower. In addition, the  
processes are highly technically complex and corres-  
pondingly expensive.

Currently, the viscous process is preferred. In this  
20 process, the cellulose is reacted with sodium hydroxide  
solution and then with carbon disulfide. This produces a  
yellow-orange-colored cellulose xanthogenate solution  
which is extruded through a spinneret. The cellulose is  
then regenerated using precipitation and washing baths.  
25 A variety of apparatuses have had to be developed for  
this for cleaning up exhaust air and wastewater.

As early as 1936 it was discovered that cellulose is  
soluble in oxides of tertiary amines (DE 713 486);  
30 however, this discovery was not pursued further until  
30 years later. In the course of this, N-methylmorpholine  
N-oxide (NMMO) was identified as the most suitable

solvent. The cellulose dissolves therein without being chemically modified. No breakdown of the cellulose chains takes place. Preparation of the corresponding spinning solutions has also been disclosed (DD 218 104;

5 DD 298 789; US-A 4 145 532; US-A 4 196 282; US-A 4 255 300). Yarns may be produced from the solutions by extrusion into a spinning bath (DE-A 44 09 609; US-A 5 417 909). WO 95/07811 (= CA 2 149 218) also discloses a process for producing tubular cellulose films  
10 by the amine oxide process. A characteristic of this process is cooling the extruded film by cooling gas immediately below the annular gap of the extrusion die. According to EP-A 662 283, the extruded tubular film is cooled internally using liquid.

15 Recovery and purification of the NMMOs are described in DD 274 435. Since the cellulose is not chemically modified in the process, less equipment is required. In the amine oxide process, no gaseous or aqueous waste  
20 products are produced, so that there are no problems with respect to the exhaust air or the wastewater. It is therefore achieving increasing importance.

EP-A 0 686 712 describes the production of flexible  
25 cellulose fibers by the N-methylmorpholine N-oxide (NMMO) spinning process. In this process, a cellulose solution in aqueous NMMO is forced through a spinneret, conducted via an air section into an NMMO-containing aqueous precipitation bath and then washed, post-treated and  
30 dried.

According to WO 93/13670, a seamless tubular food casing

is produced by extruding a solution of cellulose in NMMO/water using a special extrusion die. An air section is situated between extrusion die and precipitation bath. A characteristic of this process is a specially shaped  
5 hollow mandrel through which the precipitation liquid can also circulate in the interior of the tube. In the air section, the interior of the extruded tube is virtually completely filled by a hollow mandrel and precipitation liquid. The film is not stretched transversely in the  
10 course of this.

WO 95/35340 describes a process for producing blown cellulose films in which an underivatized cellulose dissolved in NMMO is used.

15 However, the amine oxide process also has disadvantages. The underivatized cellulose molecules are already preorientated in the NMMO solution and are substantially more tightly packed than is the case with chemically  
20 modified ("derivatized") molecules. On extrusion, the orientation in the longitudinal direction is still more pronounced. The yarns thus produced therefore exhibit a high strength in the longitudinal direction, but only low strength in the transverse direction. They have a strong  
25 tendency to split on being mechanically stressed in the wet state. Films or other shaped bodies, which must be able to be loaded in the longitudinal and transverse direction, may thus scarcely be produced by this method.

30 The object was therefore to modify the amine oxide process in such a manner that sufficiently load-bearing films or shaped bodies, in particular tubular food

casings, can be produced. The process should succeed in this case with as few steps as possible, and should remain inexpensive and environmentally compatible.

- 5    The object can be achieved if the wet treatment is combined with a blow molding. The present invention thus relates to a seamless tubular cellulose-based film, which is obtainable by extruding a cellulose-, N-methylmorpholine N-oxide- and water-containing spinning  
10    solution through an annular die and treating the tubular film in an N-methylmorpholine N-oxide-containing aqueous spinning bath, which comprises the film being longitudinally stretched by blow molding in an air section between annular gap and surface of the spinning  
15    bath.

The spinning solution preferably comprises 7 to 15% by weight, particularly preferably 9 to 12% by weight, cellulose, in each case based on the total weight of the  
20    spinning solution. The mean degree of polymerization of the cellulose in this case is preferably 300 to 700, particularly preferably 400 to 650. As solvent, the spinning solution preferably comprises 90.5 to 92.5% by weight NMNO and 9.5 to 7.5% by weight water. The  
25    parameters mentioned in this paragraph, together with the temperature, essentially determine the viscosity and fluid behavior of the spinning solution.

Processes for preparing the spinning solution are generally familiar to those skilled in the art. Customarily, cellulose is mashed in a 60% strength by weight aqueous NMNO solution at room temperature. The cellulose usually

originates from wood or cotton. As the temperature increases, water is then distilled off in a heated stirred tank under reduced pressure until the residue consists of cellulose and NMNO monohydrate. This is the  
5 case at an NMNO content of 87.7% by weight, based on the total weight of NMNO and water. The ratio of NMNO to water may be readily determined by the refractive index. In the NMNO monohydrate, the cellulose dissolved completely at a temperature of 85 to 95°C with intensive  
10 stirring. The refractive index of the solution is 1.4910 to 1.4930. The water content has decreased to 7.5 to 9.5% by weight. The spinning solution is degassed, filtered and transferred to the spinning vessel.

- 15 Food casings having improved suppleness may be obtained if modifying compounds are added to the spinning solution. The compounds must be miscible with the cellulose/NMNO/water solution. The content of these compounds is generally 0.2 to 50% by weight, preferably  
20 0.5 to 20% by weight, particularly preferably 1 to 15% by weight, in each case based on the weight of the cellulose. The compounds may be mixed homogeneously with the spinning solution at a temperature of 85 to 105°C, preferably 90 to 100°C. Particularly suitable modifying  
25 compounds are starch, starch derivatives and cellulose derivatives (in particular esters or ethers of the starch or cellulose), as well as sugar esters, and in addition hydrophilic naturally occurring polymers (preferably alginic acid and alginates, chitosan and carrageenan).  
30 Suitable compounds are also hydrophilic synthetic polymers (preferably vinyl alcohol, vinyl acetates and acrylates) and polymers which simultaneously possess

hydrophilic and hydrophobic properties (preferably esters from a sugar - such as sucrose - and fatty acids, the esters having an HLB of 1 to 15; HLB = hydrophilic-lipophilic balance). If appropriate, ethoxylated fatty acids and salts thereof, for example stearic acid or calcium stearate, waxes and paraffins are also suitable.

Finally, polyvinylpyrrolidone, copolymers of vinylpyrrolidone and 2-(dimethylamino)ethyl methacrylate, copolymers of methyl vinyl ether and maleic anhydride or of methyl vinyl ether and maleic acid monoalkyl ester may also be used. The modifying compounds may also be crosslinkable, as is the case with polyethyleneimines. These compounds generally increase the suppleness, strength, clipping stability and shear stability of the shaped bodies according to the invention. They also act as internal (primary) plasticizers. Impregnation with secondary plasticizers (such as glycerol) can frequently be even entirely omitted if the content of the modifying compounds in the food casings according to the invention is great enough (generally of the order of magnitude 8% by weight or more, based on the weight of the dry cellulose). Furthermore, they generally decrease the tendency of the cellulose to crystallize.

The spinning solution is extruded through the annular die preferably at a temperature of 85 to 105°C, particularly preferably 90 to 95°C. The annular gap is generally 0.1 to 2.0 mm wide, preferably 0.2 to 1.0 mm. The width here must be adapted to the warpage. "Warpage" is defined as the quotient of the velocity on leaving the annular gap (exit velocity) and the velocity at which the extruded tube is taken off (take-off velocity). The warpage is

generally 3.0 to 0.10, preferably 2.0 to 0.2, particularly preferably 1 to 0.4. The exit velocity, depending on the construction of the plant, is 5 to 120 m/min, preferably 10 to 80 m/min. It is also 5 determined by the caliber. On the extruded tube, advantageously, only a low tension is exerted in the longitudinal direction, which is essentially due to its own weight.

- 10 The "air section", i.e. the section between annular gap and surface of the spinning bath in which the blow molding takes place, is preferably 1 to 50 cm, particularly preferably 2.5 to 20 cm. It is also dependent on the diameter ("caliber") of the tubular film after the blow 15 molding. In contrast to the abovementioned WO 95/07811 and EP-A 662 283, no measures are required for additional cooling in the air section, and accordingly they are also not provided. The extruded tube cools only a small amount in the air section. Otherwise, transverse stretching 20 would scarcely be possible. The blow molding is effected by compressed air or other gases which pass into the interior of the tube through orifices in the die body. Stretching in the transverse direction considerably increases the transverse strength of the tube. Depending 25 on warpage, the diameter of the blow-molded tube is up to 100% greater or up to 50% smaller, preferably up to 80% greater or up to 20% smaller, than immediately after exiting the annular gap. Transverse stretching with a diameter simultaneously becoming smaller is obviously 30 only possible if the warpage is less than 1. Preferably, the diameter of the blow-molded tube is 10 to 100% greater, particularly preferably 20 to 80% greater than

immediately after exiting the annular gap.

If appropriate, the tube is conducted via a pipe, preferably a metal pipe. The diameter of this pipe can be  
5 selected between 30% greater and 30% smaller than that of the annular gap. Precipitation liquid and support air are fed via this pipe.

After entering the spinning bath, the diameter of the tube decreases. Through appropriate apparatuses in the  
10 die body, the spinning bath solution also passes into the interior of the cellulose tube. As a result, the tube solidifies more rapidly; at the same time, the insides are prevented from sticking together. The liquid level in  
15 the interior of the tube should not be significantly higher or lower than that of the surrounding spinning bath. The spinning bath itself is an aqueous solution which comprises 5 to 50% by weight, preferably 8 to 20% by weight, of NMMO. The temperature of the spinning bath  
20 is in the range from 0 to 50°C, preferably 2 to 20°C.

The depth of the spinning bath is determined by the caliber of the cellulose tube, its wall thickness and the desired residence time in the bath. Generally, the depth  
25 should be selected so that, on flattening the tube on the guide roll, the resulting edges are not damaged. In the case of a tube of caliber 20, which, immediately after leaving the annular gap, has a wall thickness of 0.5 mm and passes through the bath at a velocity of 20 m per  
30 minute, the spinning bath has a depth of about 3 m.

For further solidification, the laid-flat tube then

- passes through still more NMMO-containing precipitation vats. The first precipitation vat comprises approximately 10 to 20% by weight of NMMO. In the following precipitation vat, the NMMO content decreases. It has 5 been found to be favorable to increase the temperature from one precipitation vat to the next, up to about 60 to 70°C in the last vat. The NMMO content in the tube is thus more greatly decreased.
- 10 This so-called "precipitation section" is followed by water-filled wash vats, in which the last traces of NMMO are removed from the tube. The temperature of these baths is 15 to 70°C, preferably 40 to 60°C. Generally, a so-called plasticizer vat then follows. This comprises an 15 aqueous solution of a plasticizer for cellulose. Suitable plasticizers are polyols and polyglycols, in particular glycerol. The aqueous solution comprises 5 to 30% by weight, preferably 6 to 15% by weight, of plasticizer. The temperature of the plasticizer solution is 20 advantageously 20 to 80°C, preferably 30 to 70°C. The glycerol content of the casing is then about 15 to 30% by weight, preferably 18 to 23% by weight, in each case based on its total weight.
- 25 Thereafter, the tubes are conducted through a hot-air dryer in the inflated state. Expediently, drying is performed at decreasing temperature (from about 150°C at the inlet to about 80°C at the outlet of the dryer). An additional transverse orientation may be achieved, if 30 appropriate, by appropriately increased internal pressure on drying. Otherwise, the tube is inflated on drying to the original caliber, in order to retain the degree of

transverse orientation once achieved. During drying, the swelling value decreases to 130 to 180%, preferably 140 to 170%, depending on drying conditions and glycerol content. The tube is then wetted until the water content  
5 is 8 to 20% by weight, preferably 16 to 18% by weight, in each case based on the total weight of the tube. Then, using a pinch-roll pair, it can be laid flat and wound up.

10 Used aqueous NMMO solution may be purified by ion-exchange columns. The water can be taken off under reduced pressure until the NMMO concentration has reached 60% by weight. This NMMO solution can then be used again for preparing the spinning solution. The NMMO is thus  
15 virtually completely recovered.

Depending on caliber, the finished tubes, at a glycerol content of 20 to 22% by weight and a water content of 8 to 10% by weight, in each case based on the total weight  
20 of the tube, have a weight of 30 to 120 g/m<sup>2</sup>, preferably 35 and 80 g/m<sup>2</sup>. The weight per unit area generally increases with increasing caliber. The bursting pressure is likewise dependent on the caliber (small calibers have a higher bursting pressure). For a tube having a caliber  
25 of 16 mm, the bursting pressure is about 60 kPa, for a caliber of 30 mm about 40 kPa, at a caliber of 50 mm about 24 kPa and at a caliber of 140 mm about 15 kPa. The bursting pressure is measured in each case here in the wet state.

30 The tubular casings according to the invention can, furthermore, be provided on the inside and/or outside

with an impregnation or coating, e.g. a liquid smoke impregnation or an "easy peel" internal preparation. The same obviously applies to flat films.

- 5 An essential advantage of the flat or tubular films according to the invention is the uniform structure and thus uniform density which is achieved on precipitation. Films which are produced by the viscose process, in contrast, have a density gradient (higher density on the  
10 surface, lower in the interior).

- The tubular films according to the invention are preferably used as sausage casings, in particular as "peelable casing" in the production of frankfurters. In addition,  
15 they can also be used as membranes for various purposes, e.g. in hemodialysis. Finally, flat films can also be produced by cutting open the tubes.

- If the cellulose tubes are used as sausage casings, the  
20 stuffing caliber can correspond to the annular gap diameter or up to 120% above it. Preferably, the stuffing caliber is 10 to 80% above the annular gap diameter.

- The following examples serve for more detailed description of the invention. Percentages therein are percentages by weight, unless stated otherwise. Flat width, weight of the casing and thickness of the casing wall were determined under standard conditions (55% relative humidity; 23°C).  
25

30

Example 1:

510 g of ground wood cellulose (<sup>8</sup>Cellunier F from

Rayonier) having a mean degree of polymerization of 535 (determined by the Cuoxam method) was mashed in 5087 g of a 60% strength NMMO solution. The pH of the mash was then adjusted to 11 by NaOH. Under reduced pressure, with  
5 stirring and heating, water was then distilled off with increasing temperature, until, at an NMMO content of 87.7%, based on the total weight of water and NMMO, the monohydrate was present (recognizable by a refractive index of 1.4820). During this phase which lasted for  
10 approximately 4 hours, the vacuum was kept at 10 to 16 mmHg. After stirring for a further 2 to 3 hours, the cellulose was completely dissolved at about 85 to 95°C. In order that relatively little water is evaporated, the vacuum was set to about 200 mmHg during this time. The  
15 refractive index then ranged from about 1.4910 to 1.4930, which corresponds to a water content of 7.5 to 9%.

The spinning solution prepared in this manner was extruded at a temperature of 90°C through an annular die  
20 at a gap diameter of 20 mm and a gap width of 0.5 mm. The tube first passed through an air section about 10 cm in length at a velocity of 20 m/min. In the course of this it was transversely stretched by air fed internally. It then passed through a spinning bath section of 3 m. The  
25 spinning bath comprised a 14% strength NMMO solution which was cooled to 5°C. A solution of the same composition was also introduced into the tube interior ("inner bath"). The tube was then laid flat at a guide roll in the spinning vat. The tube had been stretched  
30 transversely to the extent that its flat width after leaving the spinning vat was 30 mm. The edges showed no damage.

The tube then passed through 4 precipitation vats each having 8 guide rolls at the top and bottom, a bath depth of 1 m and an air section of 2 m. At the end of the last vat water was introduced which was conducted in counter-current. At the outlet of the first vat, the NMNO content was kept in this manner at 12 to 16%. The temperature increased up to 60 to 70°C in the last vat. After passing through this precipitation section, residues of NMNO were washed out of the tube in 4 washing vats. The temperature in these vats was likewise 60 to 70°C. Finally, the tube was conducted through a plasticizer vat which comprised a 10% strength glycerol solution having a temperature of 60°C.

At a swelling value of 290%, the finished tube absorbed 21% glycerol. The flat width on leaving the glycerol vat was still 20 mm. The tube was then dried with hot air between 2 pinch-roll pairs. The dryer had a plurality of zones of decreasing temperature. The zone at the inlet had a temperature of 120°C, and that at the outlet 80°C. Subsequently, the tube was wetted until its water content was 8 to 12% (based on the weight of cellulose) and was wound up. The bursting pressure of this tube was 52 kPa, its static extension was 20.5 mm, and its swelling value was 165%. It was then wetted to 16 to 18% and gathered in sections ("shirred to form shirred sticks").

The shirred sticks were stuffed with sausage emulsion on an automatic stuffing machine (<sup>8</sup>FrankAMatic), scalded and smoked. Thereafter, the casing was peeled by an automatic apparatus. In the scalding and smoking behavior, this peable skin was at least as good as one produced by the

viscose process.

Example 2:

- A spinning solution as described in Example 1 was  
5 extruded at a temperature of 90°C through an annular die  
45 mm in diameter and a gap width of 0.7 mm. At a  
velocity of 20 m/min, the tube formed in this manner  
passed through an air section of 15 cm in order then to  
be immersed in the spinning bath. In the air section it  
10 was stretched transversely, as described above, with  
compressed air. The spinning bath had a depth of 3 m and  
was filled with a 12% strength aqueous NMMO solution  
which had a temperature of 5°C. Spinning bath solution  
was charged into the interior of the tube. On leaving the  
15 spinning vat, the tube had a flat width of 56 mm. Its  
swelling value was 302%. It was then inflated with  
reinforcing air, so that the flat width increased again  
to 66 mm. Before being wound up, it was wetted until the  
water content was 14 to 16%, based on the weight of the  
20 dry tube. The glycerol content was 20% at a total weight  
of 56 g/m<sup>2</sup>. Swelling value was determined at 158%. The  
soaked tube had a bursting pressure of 30 kPa. Its static  
extension at an internal pressure of 15 kPa is 44 mm.
- 25 Sections of this tubular film each having a length of  
50 m were stirred to form stirred sticks, which were then  
stuffed by an automatic stuffing machine using fine  
Mettwurst emulsion to a stuffing caliber of 44 mm. The  
sausages were then matured in the usual way and smoked.  
30 The casings according to the invention showed in this  
case properties at least as good as cellulose casings  
produced by the viscose process.

Example 3:

The spinning solution described in Example 1 was extruded at a temperature of 90°C through an annular die having a die gap diameter of 26 mm and a die gap width of 0.6 mm.

5 In contrast to the two preceding examples, the die body was joined to a 50 cm-long metal pipe over which the extruded tube was conducted. At the top end of the pipe there were situated orifices for feeding compressed air ("support air") required for the transverse stretching

10 and the spinning bath solution. The air section between die gap and surface of the spinning bath was 2.5 cm. The spinning bath was filled with a 3°C, 14% strength aqueous NMMO solution. The spinning speed was 20 m/min. Sufficient support air was fed so that the tube had a flat

15 width of 40 mm on leaving the spinning vat. Further treatment was then performed as described in Example 1. After leaving the plasticizer vat, the flat width was still 28 mm. The swelling value of the plasticized tube was 286%. It was then dried in the inflated state, wetted

20 to 12 to 16% water content and wound up on a roll. The finished tube had a weight of 44 g/m<sup>2</sup>. It comprised 22% glycerol (based on its total weight) and a swelling value of 165%. Its static extension at an internal pressure of 20 kPa was 25.8 mm, and its bursting pressure (measured

25 in the wet state) was 42 kPa.

The tubes were shirred in sections to form shirred sticks and were stuffed with sausage emulsion to a stuffing caliber of 26 mm on an automatic stuffing machine. After

30 scalding and smoking in the conventional manner, the casing was peeled off on an automatic plant and the sausages were then packed in cans. The sausage casings

according to the invention complied with all requirements at least as well as the casings produced by the viscose process.

5    Example 4:

The spinning solution prepared in accordance with Example 1, which comprised about 9% cellulose, was homogeneously mixed, with stirring, with 3%, based on the weight of the cellulose, of a sucrose monostearic acid/palmitic acid ester at a temperature of 95°C. It was then (at the same temperature) extruded through an annular die having a diameter of 20 mm and a gap width of 0.5 mm. At a velocity of 20 m/min, the tube first passed through a 10 cm long air section.. In the course of this 10 it was pressurized internally with compressed air and thus transversely stretched. Further production steps 15 were identical to those described in Example 1.

The casings gathered in sections ("shirred sticks") were 20 then placed onto the automatic stuffing machine and stuffed with sausage emulsion. After scalding and smoking, the casing was peeled off by an automatic apparatus. During scalding and smoking, the casing exhibited a behavior like the casings produced by the 25 viscose process.

In the table below, the properties of a casing produced by the conventional viscose process (termed "comparison") are compared with those of two casings according to the 30 invention, the one (termed "A") comprising no modifying compounds and having been produced according to Example 1, whereas the other (termed "B") comprising 3%,

based on the weight of the cellulose, of the sugar ester mentioned in Example 4 and was produced in accordance with this example.

	Comparison	A	B
	Flat width* (mm)	29.2	26
	Weight* (g/m <sup>2</sup> )	43.8	47.3
	Thickness* ( $\mu\text{m}$ )	40	55
5	Glycerol content** (%)	20.5	20.7
	Swelling value (%)	154	165
	Ultimate tensile strength***, longitudinal (N/mm <sup>2</sup> )	1.5	22.6
	Elongation at break***, longitudinal (%)	32	29.8
10	Change in length after wetting (%) longitudinal	-0.9	-1.0
	transverse	-1.2	-1.0
	after drying		
15	again (%) longitudinal	-2.5	-3.3
	transverse	-4.0	-10.5
	Bursting pressure*** (kPa)	48	52
			50

20 \* : measured under standard conditions

\*\* : based on the total weight

\*\*\* : in the wetted state

Example 5:

- The spinning solution prepared in accordance with Example 1 was admixed with 5%, based on the weight of the cellulose, of a copolymer of methyl vinyl ether and  
5 maleic acid monobutyl ester (molar ratio 1:1) in the form of a 50% strength ethanolic solution and homogeneously mixed at a temperature of 95°C. The solution was then extruded through an annular die having a diameter of 40 mm and a gap width of 0.7 mm. The tube passed at a  
10 velocity of 20 m/min through an air section of 15 cm, within which it was transversely stretched by compressed air. The further manufacturing steps were identical to those described in Example 1.
- 15 On leaving the spinning bath, the tube had a flat width of 66 mm, which corresponds to a diameter of 42 mm. On leaving the glycerol vat, the flat width was 56 mm, and the swelling value 302%. The tube was then inflated with compressed air, so that the flat width increased again to  
20 66 mm. Before being rolled up, it was wetted again until the water content was 14 to 16%. The glycerol content was 20%, based on the total weight of the casing, and the swelling value was 158%. The wetted tube had a bursting pressure of 30 kPa and a static extension of 44 mm at  
25 15 kPa.

Sections each 50 m in length were shirred to form shirred sticks which were then mounted on an automatic stuffing machine. The casing was then mechanically stuffed with  
30 fine Mettwurst emulsion to a caliber of 44 mm, matured and smoked. The use properties corresponded to those of casings which had been produced by the viscose process.

The ultimate tensile strength (longitudinal) was 70%, the elongation at break 50%, above that of a casing likewise produced by the NMMO process, but without addition of the modifying compound. The shrinkage was 12% less than with 5 the comparison material. The modified casing could be peeled off more readily from meat sausage than the non-modified casing.

Example 6:

10 The spinning solution prepared in accordance with Example 1 was admixed with 12%, based on the weight of the cellulose, of a copolymer of vinylpyrrolidone and 2-(dimethylamino)ethyl methacrylate (molar ratio 1:1) and homogeneously mixed at a temperature of 98°C. The 15 solution was then extruded at this temperature through an annular die having a diameter of 26 mm and a gap width of 0.6 mm. At a velocity of 20 m/min, the tube passed through an air section of 50 mm, within which it was transversely stretched by compressed air, so that on 20 leaving the spinning vat it had a flat width of 40 mm. The further manufacturing steps were identical to those described in Example 1. After leaving the plasticizer vat, the flat width was 36 mm, and the swelling value 286%.

25 The tube was then dried in the inflated state, wetted to 12 to 16% and rolled up. It comprised 22% glycerol and then had a swelling value of 165%. Its weight per square meter was 44 g. The bursting pressure (in the wet state) 30 was determined as 50 kPa. The static extension at 20 kPa was 25.8 mm. The ultimate tensile strength in the wet state was 60%, and the elongation at break was 45%, over

that of an unmodified comparison material.

The tubes were stirred in sections to form stirred sticks, which were stuffed with sausage emulsion on an  
5 automatic stuffing machine to a stuffing caliber of 26 mm, scalded and smoked. The casing was then peeled off by an automatic apparatus and the sausages were packaged in cans.

10 Example 7:

Example 6 was repeated with the difference that not 12% but 20% of the copolymer of vinylpyrrolidone and 2-(dimethylamino)ethyl methacrylate were mixed with the spinning solution. The solution was extruded through an  
15 annular die having a diameter of 40 mm and a gap width of 0.6 mm. At a velocity of 28 m/min, the tube passed through an air section of 12 cm in length, within which it was transversely stretched by compressed air. The further manufacturing steps were identical to those in  
20 Example 1.

On leaving the spinning vat, the tube had a flat width of 70 mm. In contrast to the other examples, the tube here did not pass through a softener vat, and therefore was  
25 free of glycerol. After drying it was wetted until the water content was 14 to 16% and then wound up. The swelling value was 142%, the bursting pressure 42 kPa and the static extension at 15 kPa was 44 mm. The stirred tube sections could be stuffed without problems on an  
30 automatic stuffing machine.

Example 8:

The spinning solution prepared in accordance with Example 1 was admixed with 0.8%, based on the weight of the cellulose, polyvinylpyrrolidone K 70 (mean 5  $M_w$ : 200,000) and stirred at a temperature of 95°C until a homogeneous mixture had formed. The solution was then extruded through an annular die having a diameter of 80 cm and a gap width of 0.7 mm. At a velocity of 30 m/min, the tube passed through an air section 40 cm in 10 length, within which it was transversely stretched by compressed air. The further manufacturing steps were identical to those described in Example 1, but the spinning bath comprised a 10% strength NMMO solution. The glycerol vat comprised a 7% glycerol solution.

15 The tube was dried in the inflated state in such a manner that the flat width of 130 cm was not changed. After wetting to 14 to 16% water content, the tube was wound up. It was then cut on one edge. The flat film obtained 20 in this manner had a weight of 40 g/m<sup>2</sup>, a thickness of 35 µm, a glycerol content of 21%, a swelling value of 165%, an ultimate tensile strength of 20 N/mm<sup>2</sup> in the longitudinal direction and 16 N/mm<sup>2</sup> in the transverse direction, an elongation at break in the longitudinal 25 direction of 42% and in the transverse direction of 54%.

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Patent claims

1. A seamless tubular cellulose-based film, which is obtainable by extruding a cellulose-, N-methylmorpholine N-oxide- and water-containing spinning solution through an annular die and treating the tubular film in an N-methylmorpholine N-oxide-containing aqueous spinning bath, which comprises transversely stretching the film by blow molding in an air section between annular gap and surface of the spinning bath.
- 5
2. The film as claimed in claim 1, wherein the cellulose content in the solution is 7 to 15% by weight, preferably 9 to 12% by weight, in each case based on the total weight of the solution.
- 10
3. The film as claimed in claim 1 or 2, wherein the cellulose has a mean degree of polymerization of 300 to 700, preferably 400 to 650.
- 15
4. The film as claimed in one or more of claims 1 to 3, wherein the spinning solution comprises 90.5 to 92.5% by weight of NMNO and 9.5 to 7.5% by weight of water, based on the total weight of the solvent.
- 20
5. The film as claimed in one or more of claims 1 to 4, wherein the spinning solution comprises 0.2 to 50% by weight, preferably 0.5 to 20% by weight, particularly preferably 1 to 15% by weight, of modifying compounds, in each case based on the weight of the cellulose.
- 25
- 30

6. The film as claimed in claim 5, wherein the modifying compound is starch, a starch derivative or cellulose derivative, a sugar ester, alginic acid or an alginate, chitosan, carrageenan, vinyl alcohol, vinyl acetate, an acrylate, an ester of a sugar and fatty acids, the ester having an HLB value of 1 to 15, an ethoxylated or nonethoxylated fatty acid or salt thereof, wax, paraffin, polyvinylpyrrolidone, a copolymer of vinylpyrrolidone and 2-(dimethylamino)ethyl methacrylate, a copolymer of methyl vinyl ether and maleic anhydride or a copolymer of methyl vinyl ether and maleic acid monoalkyl ester.
- 5
- 10
7. The film as claimed in one or more of claims 1 to 6, wherein the spinning solution is extruded at a temperature of 85 to 105°C, preferably 90 to 95°C, through an annular die having a gap width of 0.1 to 2.0 mm, preferably 0.2 to 1.0 mm.
- 15
- 20 8. The film as claimed in one or more of claims 1 to 7, wherein the distance between annular gap and surface of the spinning bath is 1 to 50 cm, preferably 2.5 to 20 cm.
- 25 9. The film as claimed in one or more of claims 1 to 8, wherein the spinning bath is an aqueous solution which comprises 5 to 50% by weight, preferably 8 to 20% by weight, of NMNO and has a temperature of 0 to 50°C, preferably 2 to 20°C.
- 30
10. The film as claimed in one or more of claims 1 to 9, wherein the extruded tube, downstream of the

spinning bath, further passes through in each case  
a plurality of precipitation and washing baths.

11. The film as claimed in one or more of claims 1 to  
5        10, wherein it is treated with a plasticizer,  
preferably glycerol.
12. The use of the film as claimed in one or more of  
claims 1 to 11 as sausage casing, preferably as  
10        peelable casing.
13. The use of the film as claimed in claims 1 to 11 as  
flat film after cutting open the tube in the  
longitudinal direction.  
15

**DECLARATION AND POWER OF ATTORNEY**

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**MOULDED ARTICLES OF CELLULOSE HYDRATE WITH ENZYMATICALLY MODIFIED SURFACE**

the specification of which is attached hereto unless the following box is checked:

was filed on July 4, 1997 as United States Application Number or PCT International Application Number **PCT/EP97/03530** and was amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known by me to be material to patentability as defined in Title 37, Code of Federal Regulations § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a)-(d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365 (a) of any PCT International Application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

**PRIOR FOREIGN APPLICATION(S)**

NUMBER	COUNTRY	DAY/MONTH/YEAR FILED	PRIORITY CLAIMED
<b>196 28 232.2</b>	<b>Federal Republic of Germany</b>	<b>15 July 1996</b>	<b>YES</b>

I hereby claim the benefit under Title 35, United States Code §119 (e) of any United States provisional application(s) listed below:

APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365 (c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is known by me to be material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

APPLICATION SERIAL NO.	FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

I hereby appoint as my attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Stephen A. Bent, Reg. No. 29,768; David A. Blumenthal, Reg. No. 26,257; William T. Ellis, Reg. No. 26,874; John J. Feldhaus, Reg. No. 28,822; Patricia D. Granados, Reg. No. 25,735; John P. Isaacson, Reg. No. 33,715; Michael D. Kaminski, Reg. No. 32,904; Kenneth E. Krosin, Reg. No. 25,735; Eugene M. Lee, Reg. No. 32,039; Richard Linn, Reg. No. 25,144; Peter G. Mack, Reg. No. 26,001; Brian J. McNamara, Reg. No. 32,789; Sybil Meloy, Reg. No. 22,749; George E. Quillin, Reg. No. 32,792; Colin G. Sandercock, Reg. No. 31,298; Bernhard D. Saxe, Reg. No. 28,665; Charles F. Schill, Reg. No. 27,590; Richard L. Schwaab, Reg. No. 25,479; Arthur Schwartz, Reg. No. 22,115; Harold C. Wegner, Reg. No. 25,258.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issued thereon.

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